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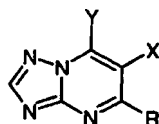
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(54) Title: FUNGICIDES



(I)

(57) Abstract: The use as a plant fungicide of a compound of general formula (I); wherein R is H, halo, C<sub>1</sub>-8? alkyl or cyano; X and Y are independently halo, C<sub>1</sub>-8? alkoxy, C<sub>1</sub>-8? alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1</sub>-4?)alkoxy, heteroaryl(C<sub>1</sub>-4?)alkoxy, aryl(C<sub>1</sub>-4?)alkylthio, heteroaryl(C<sub>1</sub>-4?)alkylthio, C<sub>1</sub>-8? alkylamino, C<sub>2</sub>-8? alkenylamino, C<sub>2</sub>-8? alkynylamino, di(C<sub>1</sub>-8?)alkylamino, di(C<sub>2</sub>-8?)alkenylamino, di(C<sub>2</sub>-8?)alkynylamino, C<sub>2</sub>-8? alkyl-(C<sub>1</sub>-8?)alkylamino or C<sub>2</sub>-8? alkenyl(C<sub>1</sub>-8?)alkylamino arylamino, aryl(C<sub>1</sub>-8? alkyl)amino, heteroaryl(C<sub>1</sub>-8? alkyl) amino, aryl(C<sub>1</sub>-4?)alkylamino, aryl(C<sub>1</sub>-4?)alkyl-(C<sub>1</sub>-8? alkyl)amino, heteroaryl(C<sub>1</sub>-4?)alkylamino, heteroaryl(C<sub>1</sub>-4?)alkyl (C<sub>1</sub>-8? alkyl)amino, morpholino or piperidino, or Y is hydroxy, provided that when X is C<sub>1</sub>-8? alkoxy, aryloxy, morpholino or piperidino, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted. Also included are plant fungicidal compositions containing these compounds and many of the compounds themselves.

WO 03/039259 A1

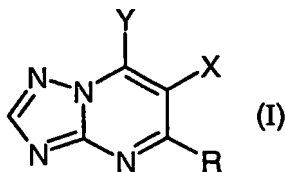
# FUNGICIDES

This invention relates to the use as plant fungicides of certain substituted *s*-1,2,4-triazolo[1,5-*a*]pyrimidine compounds. It also relates to plant fungicidal compositions containing these compounds and to many of the compounds themselves.

5 There are many substituted *s*-1,2,4-triazolo[1,5-*a*]pyrimidines known from the patent literature as being useful for controlling phytopathogenic fungi. Examples of relevant patent publications include EP-A-0071792, EP-A-0550113, US 5593996, EP-A-0834513, WO 94/20501, WO 98/46607, WO 98/46608, WO 99/48893, EP-A-0945453, WO 99/41255, US 5985883, US 5986135, US 6242451 and US 6255309. Other substituted *s*-1,2,4-triazolo[1,5-*a*]pyrimidines are described in GB-A-1148629 and by Y. Makisumi in *Chem. Pharm. Bull.* (Tokyo), 1961, 9, 801-808 & 808-814. These other triazolopyrimidines are reported as having a coronary vasodilative effect on animals (GB-A-1148629) or as being potential anticancer agents (Y. Makisuma).

15 The present invention is concerned with the provision of alternative substituted *s*-1,2,4-triazolo[1,5-*a*]pyrimidines for use as plant fungicides.

Thus, according to the present invention, there is provided the use as a plant fungicide of a compound of the general formula (I):



wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X and Y are independently halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, di(C<sub>2-8</sub>)alkenylamino, di(C<sub>2-8</sub>)alkynylamino, C<sub>2-8</sub> alkenyl-(C<sub>2-8</sub>)alkynylamino C<sub>2-8</sub> alkynyl(C<sub>1-8</sub>)alkylamino or C<sub>2-8</sub> alkenyl(C<sub>1-8</sub>)alkylamino arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino, heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino, morpholino or piperidino, or Y is hydroxy, provided that when X is C<sub>1-8</sub> alkoxy, aryloxy, morpholino or piperidino, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.

In one aspect of the invention there is provided the use as a plant fungicide of a compound of the general formula (I) wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X and Y are independently halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino or Y is hydroxy, morpholino or piperidino, provided that when X is other than halo, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.

More specifically, there is provided the use as a plant fungicide of a compound of the general formula (I) wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X is halo, C<sub>1-8</sub> alkylthio, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino; and Y is halo, hydroxy, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.

The compounds of the invention may contain one or more asymmetric carbon atoms and may exist as enantiomers (or as pairs of diastereoisomers) or as mixtures of such. However, these mixtures may be separated into individual isomers or isomer pairs, and this invention embraces such isomers and mixtures thereof in all proportions. It is to be expected that for any given compound, one isomer may be more fungicidally active than another.

Except where otherwise stated, alkyl groups and alkyl moieties of alkoxy, alkylamino, etc., suitably contain from 1 to 6, typically from 1 to 4, carbon atoms in the form of straight or branched chains. Examples are methyl, ethyl, *n*- and *iso*-propyl, *n*-, *sec*-, *iso*- and *tert*-

butyl, *n*-pentyl and *n*-hexyl. Examples of suitable optional substituents of alkyl groups and moieties include halo, hydroxy, C<sub>1-4</sub> alkoxy and C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkoxy. Where the optional substituent is halo, the haloalkyl group or moiety is typically trichloromethyl or trifluoromethyl.

5 Alkenyl and alkynyl moieties also suitably contain from 1 to 6, typically from 1 to 4, carbon atoms in the form of straight or branched chains. Examples are allyl, 2-methylallyl and propargyl. Optional substituents include halo, typically fluoro, for example, 2,2,2-trifluoro-1-methylethyl.

Halo includes fluoro, chloro, bromo and iodo. Most commonly it is fluoro, chloro or  
10 bromo.

Aryl is usually phenyl but also includes naphthyl, anthryl and phenanthryl.

Heteroaryl is typically a 5- or 6-membered aromatic ring containing one or more O, N or S heteroatoms, which may be fused to one or more other aromatic or heteroaromatic rings, such as a benzene ring. Examples are thienyl, furyl, pyrrolyl, isoxazolyl, oxazolyl,  
15 oxadiazolyl, pyrazolyl, imidazolyl, triazolyl, isothiazolyl, tetrazolyl, thiadiazolyl, pyridyl, pyrimidinyl, pyrazinyl, pyridazinyl, triazinyl, benzofuryl, benzothienyl, dibenzofuryl, benzothiazolyl, benzoxazolyl, benzimidazolyl, indolyl, quinolinyl and quinoxalinyl groups and, where appropriate, N-oxides thereof.

Any of the aryl or heteroaryl values are optionally substituted by one or more,  
20 typically 1, 2 or 3, substituents of the kind that are customarily present in pesticidal compounds. Substituents which may be present include one or more of the following: halo, hydroxy, mercapto, C<sub>1-8</sub> alkyl (especially methyl and ethyl), C<sub>2-6</sub> alkenyl (especially allyl), C<sub>2-6</sub> alkynyl (especially propargyl), C<sub>1-6</sub> alkoxy (especially methoxy), C<sub>2-6</sub> alkenyloxy (especially allyloxy), C<sub>3-6</sub> alkynyloxy (especially propargyloxy), halo(C<sub>1-8</sub>)alkyl (especially  
25 trifluoromethyl), halo(C<sub>1-6</sub>)alkoxy (especially trifluoromethoxy), C<sub>1-6</sub> alkylthio (especially methylthio), hydroxy(C<sub>1-6</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub>alkoxy(C<sub>1-4</sub>)alkoxy, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, optionally substituted aryl (especially optionally substituted phenyl), optionally substituted heteroaryl (especially optionally substituted pyridyl or pyrimidinyl), optionally substituted aryloxy (especially optionally substituted  
30 phenoxy), optionally substituted heteroaryloxy (especially optionally substituted pyridyloxy or pyrimidinyloxy), optionally substituted arylthio (especially optionally substituted phenylthio), optionally substituted heteroarylthio (especially optionally substituted

pyridylthio or pyrimidinylthio), optionally substituted aryl(C<sub>1-4</sub>)alkyl (especially optionally substituted benzyl, optionally substituted phenethyl and optionally substituted phenyl n-propyl), optionally substituted heteroaryl(C<sub>1-4</sub>)alkyl (especially optionally substituted pyridyl- or pyrimidinyl(C<sub>1-4</sub>)alkyl), optionally substituted aryl(C<sub>2-4</sub>)alkenyl (especially  
 5 optionally substituted phenylethenyl), optionally substituted heteroaryl(C<sub>2-4</sub>)alkenyl (especially optionally substituted pyridylethenyl or pyrimidinylethenyl), optionally substituted aryl(C<sub>1-4</sub>)alkoxy (especially optionally substituted benzyloxy and phenethyloxy), optionally substituted heteroaryl(C<sub>1-4</sub>)alkoxy (especially optionally substituted pyridyl- or pyrimidinyl(C<sub>1-4</sub>)alkoxy), optionally substituted aryloxy(C<sub>1-4</sub>)alkyl (especially phenoxy-  
 10 methyl), optionally substituted heteroaryloxy(C<sub>1-4</sub>)alkyl (especially optionally substituted pyridyloxy or pyrimidinyl(C<sub>1-4</sub>)alkyl), optionally substituted aryl(C<sub>1-4</sub>)alkylthio (especially optionally substituted benzylthio and phenethylthio), optionally substituted heteroaryl(C<sub>1-4</sub>)alkylthio (especially optionally substituted pyridyl or pyrimidinyl(C<sub>1-4</sub>)-alkylthio), optionally substituted arylthio(C<sub>1-4</sub>)alkyl (especially phenylthio- methyl),  
 15 optionally substituted heteroarylthio(C<sub>1-4</sub>)alkyl (especially optionally substituted pyridylthio- or pyrimidinylthio(C<sub>1-4</sub>)alkyl), acyloxy, including C<sub>1-4</sub> alkanoyloxy (especially acetyloxy) and benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, NR'R'', -NHCOR', -NHCONR'R'', -CONR'R'', -COOR', -SO<sub>2</sub>R', -OSO<sub>2</sub>R', -COR', -CR'=NR'' or -N=CR'R'' in which R' and R'' are independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo-  
 20 (C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy.

Substituents which may be present in the aryl or heteroaryl rings of any of the foregoing substituents include one or more of the following: halo, hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub>, alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>3-4</sub> alkynyloxy, halo-  
 25 (C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub>alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, alkanoyloxy, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, -NR'R'', -NHCOR', -NHCONR'R'', -CONR'R'', -COOR', -SO<sub>2</sub>R', -OSO<sub>2</sub>R', -COR', -CR'=NR'' or -N=CR'R'', in which R' and R'' have the meanings given above.

30 Typically R is H, halo or C<sub>1-4</sub> alkyl. Usually it is methyl or chloro.

When one of X or Y is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)-alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, arylamino,

aryl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino the other is suitably halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, C<sub>1-8</sub> alkylamino, di(C<sub>1-8</sub>)-alkylamino, or, in the case of Y, hydroxy.

5 In another aspect the invention provides the use as a plant fungicide of a compound of the general formula (I) wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X is halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, C<sub>1-8</sub> alkylamino or di(C<sub>1-8</sub>)alkylamino and Y is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)-alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino,  
 10 arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)-alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino, heteroaryl(C<sub>1-4</sub>)-alkyl(C<sub>1-8</sub> alkyl)amino, morpholino or piperidino; any of the foregoing alkyl moieties being optionally substituted with halo and any of the foregoing aryl or heteroaryl groups being optionally substituted with halo, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy,  
 15 cyano, nitro, amino, C<sub>1-4</sub> alkylamino or di(C<sub>1-4</sub>)alkylamino. In this aspect, R is typically halo or C<sub>1-4</sub> alkyl and X is typically halo (especially bromo), C<sub>1-4</sub> alkoxy or C<sub>1-4</sub> alkylthio. Aryl is usually phenyl and heteroaryl is, for example, pyridyl, pyrimidinyl, thienyl or imidazolyl. Typically Y is C<sub>1-4</sub> alkylamino, halo(C<sub>1-4</sub>)alkylamino, C<sub>2-4</sub> alkenylamino, halo(C<sub>2-4</sub>)-alkenylamino, C<sub>2-4</sub> alkynylamino, halo(C<sub>2-4</sub>)alkynylamino, benzyloxy, benzylamino,  
 20 heteroaryl(C<sub>1-3</sub>)alkylamino where the heteroaryl moiety is, for example, pyridyl, thienyl or imidazolyl and the phenyl moieties of the benzyl groups and the heteroaryl moieties are optionally substituted with halo, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, cyano or nitro.

In yet another aspect the invention provides the use as a plant fungicide of a  
 25 compound of the general formula (I) wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano X is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)-alkylamino, or heteroaryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino; and Y is halo, hydroxy, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, C<sub>1-8</sub> alkylamino or di(C<sub>1-8</sub>)alkylamino; any of the foregoing alkyl moieties being optionally substituted with halo and any of the foregoing aryl or heteroaryl groups

being optionally substituted with halo, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, cyano, nitro, amino, C<sub>1-4</sub> alkylamino or di(C<sub>1-4</sub>)alkylamino. In this aspect, R is typically halo or C<sub>1-4</sub> alkyl and Y is typically halo (especially chloro), hydroxy, C<sub>1-4</sub> alkylamino or halo(C<sub>1-4</sub>)alkylamino. Aryl is usually phenyl and heteroaryl is, for example, pyridyl, pyrimidinyl, thienyl or imidazolyl. Typically X is phenylthio or heteroarylthio where the heteroaryl moiety is, for example, pyridyl, thienyl or imidazolyl and the phenyl and heteroaryl moieties are optionally substituted with halo, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, cyano or nitro.

In yet another aspect the invention provides the use as a plant fungicide of a compound of the general formula (I) wherein R is halo (e.g. chloro); X is phenoxy, phenylthio, heteroaryloxy (e.g. pyridyloxy and pyrimidinylloxy), heteroarylthio (e.g. pyridinylthio and pyrimidinylthio), morpholino or piperidino; and Y is C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, di(C<sub>2-8</sub>)alkenylamino, di(C<sub>2-8</sub>)alkynylamino, C<sub>2-8</sub> alkenyl(C<sub>2-8</sub>)alkynylamino C<sub>2-8</sub> alkynyl(C<sub>1-8</sub>)alkylamino or C<sub>2-8</sub> alkenyl(C<sub>1-8</sub>)alkylamino; any of the foregoing alkyl, alkenyl, alkynyl, phenyl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted. Halo, especially fluoro, is a typical substituent of alkyl, alkenyl and alkynyl and halo (e.g. chloro and fluoro), C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl (e.g. trifluoromethyl), C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy (e.g. trifluoromethoxy) and nitro are typical substituents of phenyl and heteroaryl groups. Exemplary values of Y are 2,2,2-trifluoro-1-methylethylamino and *N*-ethyl-2-methylallylamino.

In yet another aspect the invention provides the use as a plant fungicide of a compound of the general formula (I) wherein R is halo (e.g. chloro); X is phenylthio, heteroaryloxy (e.g. pyridyloxy and pyrimidinylloxy) or heteroarylthio (e.g. pyridinylthio and pyrimidinylthio); and Y is halo (e.g. chloro); any of the foregoing phenyl or heteroaryl moieties being optionally substituted, for example, with the substituents described in the previous paragraph.

The invention also includes those compounds of general formula (I) that are novel. Thus in yet another aspect the invention provides a compound of general formula (I) wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X and Y are independently halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub>

- alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino or Y is hydroxy, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted; provided that when X is other than halo, R and Y are not both halo, that when X is bromo and R is methyl, Y is not diethylamino or 3-(diethylamino)-propylamino, that when X is chloro and R is methyl, Y is not benzylamino and that when X is bromo or chloro and R is H or methyl, Y is not chloro or hydroxy.
- More specifically, the invention includes a compound of the general formula (I) wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X is halo, C<sub>1-8</sub> alkylthio, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino; and Y is halo, hydroxy, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted; provided that when X is bromo and R is methyl, Y is not diethylamino or 3-(diethylamino)-propylamino, that when X is chloro and R is methyl, Y is not benzylamino and that when X is bromo or chloro and R is H or methyl, Y is not chloro or hydroxy.

The invention also includes a compound of the general formula (I) wherein R is halo (e.g. chloro); X is phenoxy, phenylthio, heteroaryloxy (e.g. pyridyloxy and pyrimidinylloxy), heteroarylthio (e.g. pyridinylthio and pyrimidinylthio), morpholino or piperidino; and Y is C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, di(C<sub>2-8</sub>)alkenylamino, di(C<sub>2-8</sub>)alkynylamino, C<sub>2-8</sub> alkenyl(C<sub>2-8</sub>)alkynylamino, C<sub>2-8</sub> alkynyl(C<sub>1-8</sub>)alkylamino or C<sub>2-8</sub> alkenyl(C<sub>1-8</sub>)alkylamino; any of the foregoing alkyl, alkenyl, alkynyl, phenyl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.



Halo, especially fluoro, is a typical substituent of alkyl, alkenyl and alkynyl and halo (e.g. chloro and fluoro), C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl (e.g. trifluoromethyl), C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy (e.g. trifluoromethoxy) and nitro are typical substituents of phenyl and heteroaryl groups. Exemplary values of Y are 2,2,2-trifluoro-1-methylethylamino and *N*-ethyl-2-methylallylamino.

The invention further includes a compound of the general formula (I) wherein R is halo (e.g. chloro); X is phenylthio, heteroaryloxy (e.g. pyridyloxy and pyrimidinylloxy) or heteroarylthio (e.g. pyridinylthio and pyrimidinylthio); and Y is halo (e.g. chloro); any of the foregoing phenyl or heteroaryl moieties being optionally substituted, for example, with the substituents described in the previous paragraph.

The further definitions of compound (I) detailed above in relation to its use as a fungicide (including specified usual, typical, suitable and exemplary values), apply equally to the invention compounds themselves.

Compounds that form part of the invention are illustrated in Table 1 below. The compounds have the general formula (I) with the values of R, X and Y given in the table.

Table 1

Compound No.	R	X	Y	Melting Point (°C)	Mass Ion (M <sup>+</sup> /M+1 <sup>+</sup> )
1	CH <sub>3</sub>	Br	NHCH(CH <sub>3</sub> ) <sub>2</sub>		270
2	CH <sub>3</sub>	Br	NHCH <sub>2</sub> CF <sub>3</sub>		310
3	CH <sub>3</sub>	S-4-F-phenyl	Cl		295
4	CH <sub>3</sub>	S-5-CF <sub>3</sub> -pyrid-2-yl	OH		328
5	CH <sub>3</sub>	SCH <sub>3</sub>	NHCH <sub>2</sub> CF <sub>3</sub>		278
6	CH <sub>3</sub>	S-4-F-phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>	oil	318
7	CH <sub>3</sub>	I	OH		277
8	Cl	Br	Cl		267
9	CH <sub>3</sub>	Br	OCH <sub>2</sub> -2,4,6-F <sub>3</sub> -phenyl	202-4	374
10	CH <sub>3</sub>	Br	NHCH <sub>2</sub> -4-F-phenyl		338
11	CH <sub>3</sub>	Br	Morpholino		299
12	CH <sub>3</sub>	Br	Piperidino		297
13	CH <sub>3</sub>	Br	OCH <sub>2</sub> -3-CF <sub>3</sub> -phenyl		388
14	CH <sub>3</sub>	Br	OCH <sub>2</sub> -F <sub>5</sub> -phenyl		410
15	CH <sub>3</sub>	Br	OCH <sub>2</sub> -4-CN-phenyl		345
16	CH <sub>3</sub>	Br	OCH <sub>2</sub> -3-NO <sub>2</sub> -phenyl		365
17	CH <sub>3</sub>	Br	NH(CH <sub>2</sub> ) <sub>3</sub> -imidazol-1-yl		338
18	CH <sub>3</sub>	Br	NHCH <sub>2</sub> -pyrid-2-yl		321
19	CH <sub>3</sub>	Br	NHCH <sub>2</sub> C≡CH		268

20	CH <sub>3</sub>	Br	NHCH <sub>2</sub> -thien-3-yl		326
21	Cl	S-4-F-phenyl	Cl		
22	Cl	Piperidino	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>	127	
23	Cl	Piperidino	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )	133	
24	Cl	S-5-CF <sub>3</sub> -pyrid-2-yl	Cl		
25	Cl	Morpholino	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>	amorph	351
26	Cl	Morpholino	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )	amorph	337
27	Cl	S-3-NO <sub>2</sub> -phenyl	Cl		
28	Cl	O-4-F-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>	156	
29	Cl	O-4-F-phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )	90	
30	Cl	S-3,4,5-F <sub>3</sub> -phenyl	Cl	218	
31	Cl	O-3,4,5-F <sub>3</sub> -phenyl	(R)-NHCHCH <sub>3</sub> CF <sub>3</sub>	128	
32	Cl	O-3,4,5-F <sub>3</sub> -phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )	169	
33	Cl	S-2-NO <sub>2</sub> -phenyl	Cl		
34	Cl	O-2-NO <sub>2</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>	amorph	403
35	Cl	O-2-NO <sub>2</sub> -phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )	amorph	489
36	Cl	S-4-MeO-phenyl	Cl		
37	Cl	O-4-MeO-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		388
38	Cl	O-4-MeO-phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )		374
39	Cl	O-2-pyridyl	Cl		282
40	Cl	O-2-pyridyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		359
41	Cl	O-2-pyridyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )		345
42	Cl	S-2-F-phenyl	Cl		
43	Cl	O-2-F-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		376
44	Cl	O-2-F-phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )		362
45	Cl	S-2-CH <sub>3</sub> -phenyl	Cl		
46	Cl	O-2-CH <sub>3</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		372
47	Cl	O-2-CH <sub>3</sub> -phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )		358
48	Cl	S-2,6-F <sub>2</sub> -phenyl	Cl		
49	Cl	O-2,6-F <sub>2</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		394
50	Cl	O-2,6-F <sub>2</sub> -phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )		380
51	Cl	O-2,4,6-F <sub>3</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>	185	
52	Cl	O-2,4,6-F <sub>3</sub> -phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )	203	
53	Cl	O-1-naphthyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		408
54	Cl	O-1-naphthyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )		394
55	Cl	O-2-MeO-5-Br-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		466
56	Cl	O-2-MeO-5-Br-phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )		452
57	Cl	S-2-MeO-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>	123	
58	Cl	S-2-MeO-phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )	101	
59	Cl	S-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		374
60	Cl	S-phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )		360
61	Cl	O-2-CF <sub>3</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		442
62	Cl	O-2-CF <sub>3</sub> -phenyl	N(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> )	101	
63	Me	Morpholino	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		

64	Me	Morpholino	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
65	Me	S-3-NO <sub>2</sub> -phenyl	Cl		
66	Me	O-4-F-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
67	Me	O-4-F-phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
68	Me	S-3,4,5-F <sub>3</sub> phenyl	Cl		
69	Me	O-3,4,5-F <sub>3</sub> -phenyl	(R)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
70	Me	O-3,4,5-F <sub>3</sub> -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
71	Me	S-2-NO <sub>2</sub> -phenyl	Cl		
72	Me	O-2-NO <sub>2</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
73	Me	O-2-NO <sub>2</sub> -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
74	Me	S-4-MeO-phenyl	Cl		
75	Me	O-4-MeO-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
76	Me	O-4-MeO-phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
77	Me	O-2-pyridyl	Cl		
78	Me	O-2-pyridyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
79	Me	O-2-pyridyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
80	Me	S-2-F-phenyl	Cl		
81	Me	O-2-F-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
82	Me	O-2-F-phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
83	Me	S-2-CH <sub>3</sub> -phenyl	Cl		
84	Me	O-2-CH <sub>3</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
85	Me	O-2-CH <sub>3</sub> -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
86	Me	S-2,6-F <sub>2</sub> -phenyl	Cl		
87	Me	O-2,6-F <sub>2</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
88	Me	O-2,6-F <sub>2</sub> -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
89	Me	O-2,4,6-F <sub>3</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
90	Me	O-2,4,6-F <sub>3</sub> -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
91	Cl	Piperidino	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
92	Cl	Piperidino	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
93	Cl	O-2-MeO-phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
94	Cl	O-2-MeO-phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
95	Cl	O-2,4,5-F <sub>3</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
96	Cl	O-2,4,5-F <sub>3</sub> -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
97	Cl	S-2,4,5-F <sub>3</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
98	Cl	S-2,4,5-F <sub>3</sub> -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
99	Cl	S-2,4,6-F <sub>3</sub> -phenyl	(S)-NHCHCH <sub>3</sub> CF <sub>3</sub>		
100	Cl	S-2,4,6-F <sub>3</sub> -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
101	Cl	O-2,6-F <sub>2</sub> -phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
102	Cl	O-2,4,6-F <sub>3</sub> -phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
103	Cl	O-2-naphthyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
104	Cl	O-2-MeO-5-Br-phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
105	Cl	S-2-MeO-phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
106	Cl	S-phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
107	Cl	O-2-CF <sub>3</sub> -phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
108	Cl	Morpholino	NHCH(CH <sub>3</sub> ) <sub>2</sub>		

109	Cl	S-3-NO <sub>2</sub> -phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
110	Cl	O-4-F-phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
111	Cl	S-3,4,5-F <sub>3</sub> phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
112	Cl	O-3,4,5-F <sub>3</sub> -phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
113	Cl	S-2-NO <sub>2</sub> -phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
114	Cl	O-2-NO <sub>2</sub> -phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
115	Cl	S-4-MeO-phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		
116	Cl	O-4-MeO-phenyl	NHCH(CH <sub>3</sub> ) <sub>2</sub>		

The compounds of formula (I) may be prepared as outlined in Routes 1 to 6 below, in which R has the meaning given above and L is a leaving group such as halo. Y is shown as  
 5 OR<sub>1</sub>, NHR<sub>1</sub>, NHR<sub>2</sub>, NR<sub>2</sub>R<sub>3</sub> or NR<sub>3</sub>R<sub>4</sub> and X is shown as OR<sub>1</sub>, SR<sub>1</sub>, SR<sub>2</sub> or NR<sub>1</sub>R<sub>2</sub>, the values of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> being derived from the meanings of X and Y given above. Hünig's base is *N,N*-diisopropylethylamine.

Thus, as shown in Route 1, compounds where Y is an amino-linked substituent (II), in which R is methyl, may be prepared by reacting a compound of general formula (III) with  
 10 the appropriate primary amine R<sub>1</sub>NH<sub>2</sub> or secondary amine R<sub>1</sub>R<sub>2</sub>NH conveniently in a solvent such as dimethyl sulphoxide at about 0°C in the presence of Hünig's base. The compound of general formula (III) may be prepared by treating a compound of general formula (IV) with phosphoryl chloride under reflux conditions. The compound of formula (IV) may be prepared by treating a compound of general formula (V) with liquid bromine at room temperature in,  
 15 for example, glacial acetic acid. The compound of general formula (V) where R is methyl is commercially available.

Compounds where Y is an *O*-linked substituent (VI) may be prepared, as shown in Route 2, by reacting a compound of formula R<sub>1</sub>-L with a compound of general formula (IV) in the presence of a suitable base

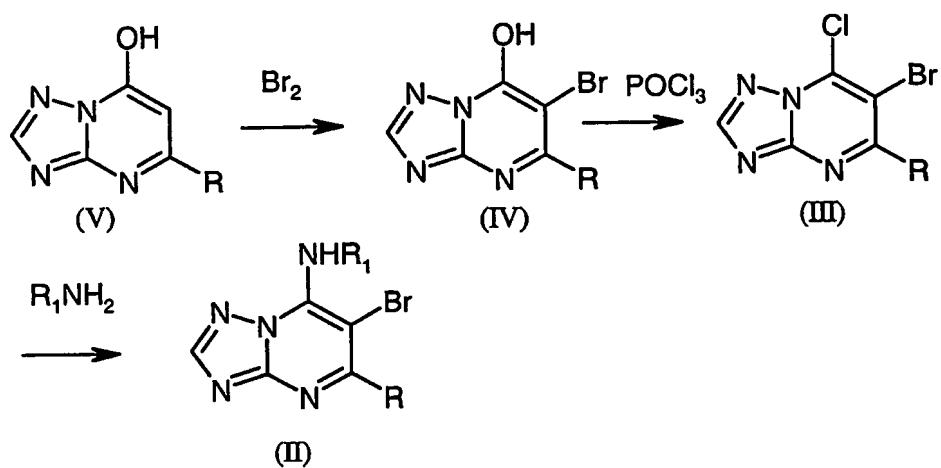
20 Compounds where X is a *S*-linked substituent and Y is an amino-linked substituent (VII) may be prepared, as shown in Route 3, by chlorinating a compound of general formula (VIII) with, for example, phosphoryl chloride followed by treatment with an amine R<sub>2</sub>NH<sub>2</sub>. The compound of general formula (VIII) may be prepared by reacting a compound of general formula (IV) with a thiol of formula R<sub>1</sub>SH.

25 Compounds where X is a *S*-linked substituent and Y is an amino-linked substituent (IX) may also be prepared, as shown in Route 4, by reacting a compound of general formula (II) with a thiol of formula R<sub>2</sub>SH.

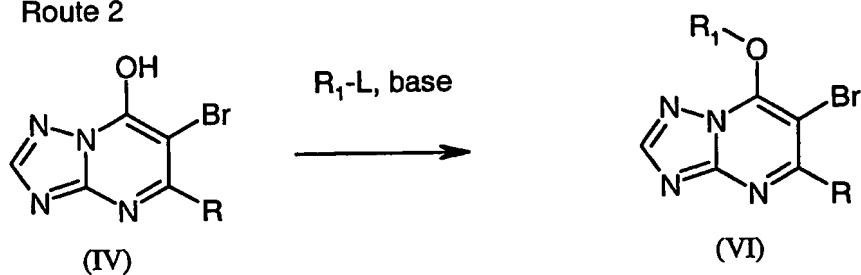
Compounds where X is an *O*-bridged substituent and Y is an amino-linked substituent (XI) may be prepared, as shown in Route 5, by chlorinating a compound of general formula (X) with, for example, phosphoryl chloride followed by treatment with an amine  $R_2R_3NH$  in DMF. The compound of general formula (X) may be prepared by reacting  
5 a compound of general formula (IV) with a phenol of formula  $R_1OH$  in the presence of a suitable base like KF or  $K_2CO_3$ .

Compounds where X is a *N*-bridged substituent and Y is an amino-linked substituent (XIII) may be prepared, as shown in Route 6, by chlorinating a compound of general formula (XII) with, for example, phosphoryl chloride followed by treatment with an amine  $R_3R_4NH$   
10 in DMF. The compound of general formula (XII) may be prepared by reacting a compound of general formula (IV) with an amine of formula  $R_3R_4NH$  in DMF.

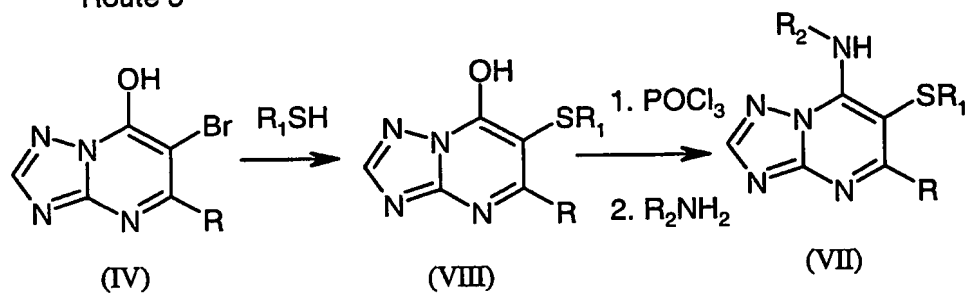
## Route 1



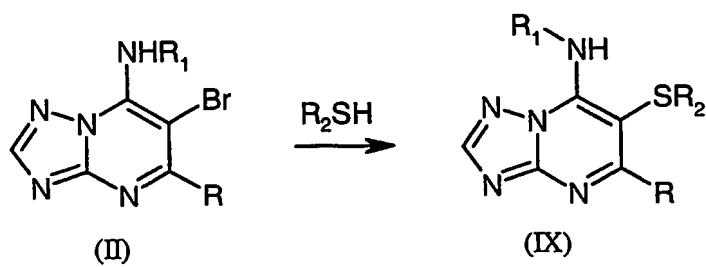
## Route 2



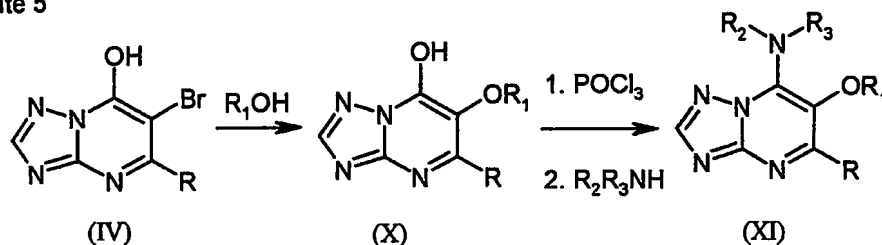
## Route 3



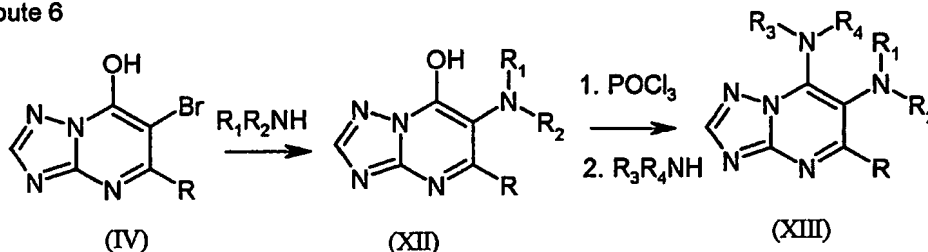
## Route 4



## Route 5



## Route 6



Other compounds of the general formula (I) may be prepared by standard methods described in the literature from the commercially available 5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (compound (V) where R is methyl) or using compounds (II), (III), (IV), (VI) or (VIII) as intermediates. Alternatively, they may be prepared from intermediates described by Y. Makisumi in *Chem. Pharm. Bull.* (Tokyo), 9, 801-808 & 808-814 by standard literature methods.

The compounds of formula (I) are active fungicides and may be used to control one or more of the following pathogens: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Puccinia triticina* (or *recondita*), *Puccinia striiformis* and other rusts on wheat, *Puccinia hordei*, *Puccinia striiformis* and other rusts on barley, and rusts on other hosts (for example turf, rye, coffee, pears, apples, peanuts, sugar beet, vegetables and ornamental plants); *Erysiphe cichoracearum* on cucurbits (for example melon); *Blumeria* (or *Erysiphe*) *graminis* (powdery mildew) on barley, wheat, rye and turf and other powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*) on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Cochliobolus* spp., *Helminthosporium* spp., *Drechslera* spp. (*Pyrenophora* spp.), *Rhynchosporium* spp., *Mycosphaerella graminicola* (*Septoria tritici*) and *Phaeosphaeria nodorum* (*Stagonospora nodorum* or *Septoria nodorum*), *Pseudocercospora herpotrichoides* and *Gaeumannomyces graminis* on cereals

(for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts;

5 *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, potatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat, cucurbits and other hosts;

10 *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat, lumber and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example bitter rot (*Glomerella cingulata*), black rot or frog-eye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomi*), Cedar apple rust

15 (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomi*) and white rot (*Botryosphaeria dothidea*)) on apples and pears; *Plasmopara viticola* on vines; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium*

20 *ultimum*) on turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts; *Thanatephorus cucumeris* on rice and turf and other *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, potatoes, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts

25 and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas, peanuts, citrus, pecans, papaya and other hosts; *Diaporthe* spp. on citrus, soybean, melon, pears, lupin and other hosts; *Elsinoe* spp. on citrus, vines, olives, pecans, roses and other hosts; *Verticillium* spp. on a range of hosts including hops, potatoes and tomatoes;

30 *Pyrenopeziza* spp. on oil-seed rape and other hosts; *Oncobasidium theobromae* on cocoa causing vascular streak dieback; *Fusarium* spp., *Typhula* spp., *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but



particularly wheat, barley, turf and maize; *Ramularia* spp. on sugar beet, barley and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*, *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis cinerea* on grapes); other pathogens on vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarius*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seeditiosum*) or lumber, notably *Cephaloascus fragrans*, *Ceratocystis* spp., *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergi* and *Aureobasidium pullulans*; and fungal vectors of viral diseases (for example *Polymyxa graminis* on cereals as the vector of barley yellow mosaic virus (BYMV) and *Polymyxa betae* on sugar beet as the vector of rhizomania).

A compound of formula (I) may move acropetally, basipetally or locally in plant tissue to be active against one or more fungi. Moreover, a compound of formula (I) may be volatile enough to be active in the vapour phase against one or more fungi on the plant.

The invention therefore provides a method of combating or controlling phytopathogenic fungi which comprises applying a fungicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other plant growth medium, e.g. nutrient solution.

The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes protectant, curative, systemic, eradicator and antispore treatments.

The compounds of formula (I) are preferably used for agricultural, horticultural and turfgrass purposes in the form of a composition.

In order to apply a compound of formula (I) to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other growth medium, a compound of formula (I) is usually formulated into a composition which includes, in addition to the compound of formula (I), a suitable inert diluent or carrier and, optionally, a surface active agent (SFA). SFAs are chemicals that are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersion, emulsification and

wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of a compound of formula (I). The composition is generally used for the control of fungi such that a compound of formula (I) is applied at a rate of from 0.1g to 10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

When used in a seed dressing, a compound of formula (I) is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed.

In another aspect the present invention provides a fungicidal composition comprising a fungicidally effective amount of a compound of formula (I) and a suitable carrier or diluent therefor.

In a still further aspect the invention provides a method of combating and controlling fungi at a locus which comprises treating the fungi or the locus of the fungi with a fungicidally effective amount of a composition comprising a compound of formula (I).

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), aerosols, fogging/smoke formulations, capsule suspensions (CS) and seed treatment formulations. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of formula (I).

Dustable powders (DP) may be prepared by mixing a compound of formula (I) with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

Soluble powders (SP) may be prepared by mixing a compound of formula (I) with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of

said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

Wettable powders (WP) may be prepared by mixing a compound of formula (I) with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of formula (I) and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of formula (I) (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of formula (I) (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrans, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

Dispersible Concentrates (DC) may be prepared by dissolving a compound of formula (I) in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of formula (I) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone), alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), N-alkylpyrrolidones (such as N-methylpyrrolidone or N-octylpyrrolidone), dimethyl amides of fatty acids (such as C<sub>8</sub>-C<sub>10</sub> fatty acid dimethylamide) and chlorinated hydrocarbons. An EC

product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment. Preparation of an EW involves obtaining a compound of formula (I) either as a liquid (if it is not a liquid at room temperature, it may be melted at a reasonable temperature, typically below 70°C) or in solution (by dissolving it in an appropriate solvent) and then emulsifying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or alkylnaphthalenes) and other appropriate organic solvents that have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of formula (I) is present initially in either the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in ECs or in EWs. An ME may be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides in the same formulation. An ME is suitable for dilution into water, either remaining as a microemulsion or forming a conventional oil-in-water emulsion.

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of formula (I). SCs may be prepared by ball or bead milling the solid compound of formula (I) in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle. Alternatively, a compound of formula (I) may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

Aerosol formulations comprise a compound of formula (I) and a suitable propellant (for example *n*-butane). A compound of formula (I) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

A compound of formula (I) may be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing the compound.

Capsule suspensions (CS) may be prepared in a manner similar to the preparation of  
5 EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of formula (I) and, optionally, a carrier or diluent therefor. The polymeric shell may be produced by either an interfacial polycondensation reaction or by a coacervation procedure. The compositions may provide for controlled release of the  
10 compound of formula (I) and they may be used for seed treatment. A compound of formula (I) may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

A composition may include one or more additives to improve the biological performance of the composition (for example by improving wetting, retention or distribution  
15 on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of formula (I)). Such additives include surface active agents, spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which may aid or modify the action of a compound of formula (I)).

20 A compound of formula (I) may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of,  
25 respectively, DP, SP, WP, SC and DC compositions described above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil or a film-forming barrier).

Wetting agents, dispersing agents and emulsifying agents may be SFAs of the cationic, anionic, amphoteric or non-ionic type.

30 Suitable SFAs of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-  
5 *isopropyl*- and tri-*isopropyl*-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and  
10 tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycines.

Suitable SFAs of the non-ionic type include condensation products of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty  
15 alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or hexitol anhydrides; condensation products of said partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine  
20 oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

A compound of formula (I) may be applied by any of the known means of applying  
25 fungicidal compounds. For example, it may be applied, formulated or unformulated, to any part of the plant, including the foliage, stems, branches or roots, to the seed before it is planted or to other media in which plants are growing or are to be planted (such as soil surrounding the roots, the soil generally, paddy water or hydroponic culture systems), directly or it may be sprayed on, dusted on, applied by dipping, applied as a cream or paste  
30 formulation, applied as a vapour or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed in a water-soluble bag) in soil or an aqueous environment.

A compound of formula (I) may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being added to water before use. These concentrates, which may include DCs, SCs, ECs, EWs, MEs SGs, SPs, WPs, WGs and CSs, are often required to withstand storage for prolonged periods and, after such storage, to be capable of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Such aqueous preparations may contain varying amounts of a compound of formula (I) (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

A compound of formula (I) may be used in mixtures with fertilisers (for example nitrogen-, potassium- or phosphorus-containing fertilisers). Suitable formulation types include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the compound of formula (I).

The invention therefore also provides a fertiliser composition comprising a fertiliser and a compound of formula (I).

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematocidal or acaricidal activity.

By including another fungicide, the resulting composition may have a broader spectrum of activity or a greater level of intrinsic activity than the compound of formula (I) alone. Further the other fungicide may have a synergistic effect on the fungicidal activity of the compound of formula (I).

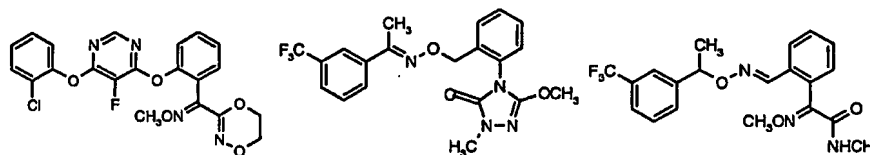
The compound of formula (I) may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the compound of

formula (I); or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition.

Examples of fungicidal compounds which may be included in the composition of the invention are AC 382042 (*N*-(1-cyano-1,2-dimethylpropyl)-2-(2,4-dichlorophenoxy) propionamide), acibenzolar-*S*-methyl, alanycarb, aldimorph, anilazine, azaconazole, azafenidin, azoxystrobin, benalaxyl, benomyl, biloxazol, bitertanol, blasticidin S, bromuconazole, bupirimate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA 41396, CGA 41397, chinomethionate, chlorbenzthiazone, chlorothalonil, chlorozolate, clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulphate, copper tallate, and Bordeaux mixture, cyamidazosulfamid, cyflufenamid, cymoxanil, cyproconazole, cyprodinil, debacarb, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, diclocymet, diclomezine, dicloran, didecyl dimethyl ammonium chloride, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O,O*-di-*iso*-propyl-*S*-benzyl thiophosphate, dimefluazole, dimetconazole, dimethirimol, dimethomorph, dimoxystrobin, diniconazole, dinocap, dithianon, dodecyl dimethyl ammonium chloride, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, ethaboxam, ethirimol, ethyl (*Z*)-*N*-benzyl-*N*-([methyl(methyl-thioethylideneaminooxycarbonyl)amino]thio)- $\beta$ -alaninate, etridiazole, famoxadone, fenamidone, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, flumorph, fluoroimide, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, iminoctadine, iminoctadine triacetate, ipconazole, iprobenfos, iprodione, iprovalicarb, isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY 248908, mancozeb, maneb, mfenoxam, mepanipyrim, mepronil, metalaxyl, metconazole, metiram, metiram-zinc, metominostrobin, metrafenone, MON65500 (*N*-allyl-4,5-dimethyl-2-trimethylsilylthiophene-3-carboxamide), myclobutanil, NTN0301, neoasozin, nickel dimethyldithiocarbamate, nicobifen, nitrothale-isopropyl, nuarimol, ofurace, organomercury compounds, oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosphorus acids, phthalide, picoxystrobin, polyoxin D, polyram, probenazole, prochloraz, procymidone,



propamocarb, propamocarb hydrochloride, propiconazole, propineb, propionic acid, prothioconazole, pyraclostrobin, pyrazophos, pyrifenoxy, pyrimethanil, pyroquilon, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinomethionate, quinoxyfen, quintozone, sipconazole, sodium pentachlorophenate, spiroxamine, streptomycin, sulphur, tebuconazole, 5 tecloftalam, tecnazene, tetraconazole, thiabendazole, thifluzamide, 2-(thiocyanomethylthio)-benzothiazole, thiophanate-methyl, thiram, tiadinil, timibenconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triflumizole, triforine, triticonazole, validamycin A, vapam, vinclozolin, XRD-563, zineb, ziram, zoxamide and compounds of the formulae:



10

The compounds of formula (I) may be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Some mixtures may comprise active ingredients which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

20

The invention is illustrated by the following Examples in which the following abbreviations are used:

ml = millilitres

nmr = nuclear magnetic resonance

g = grammes

DMSO = dimethyl sulphoxide

ppm = parts per million

DMF = *N,N*-dimethylformamide

M<sup>+</sup> = mass ion

HPLC = high performance liquid chromatography

## EXAMPLE 1

This Example illustrates the preparation of 5-methyl-6-bromo-7-trifluoroethylamino-s-1,2,4-triazolo[1,5-a]pyrimidine (Compound No. 2, Table 1)

## Stage 1

5 A solution of bromine (4.1ml) in glacial acetic acid (20ml) was added dropwise to a solution of 5-methyl-s-triazolo[1,5-a]pyrimidin-7-ol (10.0g) in glacial acetic acid (80ml) with stirring at room temperature. After complete addition, the solution was stirred at room temperature for 3 hours. The solid was separated by filtration, washed with ethanol and air dried to give 5-methyl-6-bromo-s-triazolo[1,5-a]pyrimidin-7-ol (14.8g, 98% yield) as a pale  
10 yellow solid.

$^1\text{H}$  nmr  $\delta$  2.40 (3H,s), 3.80 (1H, bs), 8.20 (1H, s) ppm.

## Stage 2

Phosphoryl chloride (25ml) was added dropwise, with caution, to 5-methyl-6-bromo-s-triazolo[1,5-a]pyrimidin-7-ol (5.0g). After complete addition the mixture was refluxed for  
15 24 hours, cooled to room temperature and poured carefully with stirring onto crushed ice. The resulting red solution was extracted with chloroform, washed with water, dried and the solvent removed to give 5-methyl-6-bromo-7-chloro-s-triazolo[1,5-a]pyrimidine (3.60g, 70% yield) as an orange solid.

$^1\text{H}$  nmr  $\delta$  2.90 (3H, s), 8.50 (1H, s) ppm.

## 20 Stage 3

2,2,2-Trifluoroethylamine (3.2ml) was added dropwise to a solution of 5-methyl-6-bromo-7-chloro-s-triazolo[1,5-a]pyrimidine (2.5g) and Hünig's base (2.6ml) in dry DMSO (25ml) at 0°C. The reaction was stirred for 3 days at room temperature, poured into ice cold water and extracted with ether. The ether extracts were washed with water, dried over  
25 anhydrous magnesium sulphate and the ether removed to give the title compound (1.35g, 43% yield) as a yellow solid ( $M^+ = 310$ ).

$^1\text{H}$  nmr  $\delta$  2.80 (3H, s), 5.00 (2H, m), 6.00 (1H,m), 8.30 (1H, s) ppm.

## EXAMPLE 2

This Example illustrates the preparation of 5-methyl-6-bromo-7-isopropylamino-s-  
30 1,2,4-triazolo[1,5-a]pyrimidine (Compound No. 1, Table 1)

Isopropylamine (0.75ml) was added dropwise to a solution of 5-methyl-6-bromo-7-chloro-s-triazolo[1,5-a]pyrimidine (1.0g) (prepared as described in Example 1, Stage 2) and

Hünig's base (1.0ml) in dry DMSO (10ml) at 0°C. The reaction mixture was stirred at room temperature for 2.5 hours, poured into ice-cold water and extracted with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulphate and the ether removed to give the title compound (0.7g, 65% yield) as a yellow powder ( $M^+ = 270$ ).

5  $^1\text{H}$  nmr  $\delta$  1.4 (6H, d), 2.7 (3H, s), 5.3 (1H, m), 5.7 (1H, d), 8.2 (1H, s) ppm.

### EXAMPLE 3

This Example illustrates the preparation of 5-methyl-6-(4-fluoro-(phenylthio))-7-isopropylamino-s-1,2,4-triazolo[1,5-a]pyrimidine (Compound No. 6, Table 1)

A mixture of 5-Methyl-6-bromo-7-isopropylamino-s-1,2,4-triazolo[1,5-a]pyrimidine  
10 (0.230g) (prepared as described in Example 2), 4-fluorothiophenol (0.128g) and anhydrous potassium carbonate (0.138g) in ethylene glycol (6ml) was stirred under a nitrogen atmosphere at 150°C for 3 hours. The reaction mixture was cooled to room temperature, poured into ice water and extracted with ethyl acetate. The ether extracts were washed with water, dried over anhydrous magnesium sulphate and the solvent removed to give a yellow  
15 oil which was purified by Bond Elute chromatography eluting with ethyl acetate/hexane 1:3 to give the title compound (0.032g, 11% yield) as a yellow oil ( $M^+ = 318$ ).

$^1\text{H}$  nmr  $\delta$  1.3 (6H, d), 2.7 (3H, s), 5.4 (1H, m), 6.4 (1H, d), 7.0 (4H, m), 8.3 (1H, s) ppm.

### EXAMPLE 4

This Example illustrates the preparation of 5-methyl-6-(4-fluoro-phenylthio)-7-chloro-s-1,2,4-triazolo[1,5-a]pyrimidine (Compound No. 3, Table 1)

#### Stage 1

A mixture of 5-methyl-6-bromo-s-triazolo[1,5-a]pyrimidin-7-ol (0.700g), 4-fluorothiophenol (0.390g) and anhydrous potassium carbonate (0.415g) in ethylene glycol (5ml) was stirred under a nitrogen atmosphere at 140-150°C for 5 hours. The reaction mixture was  
25 cooled to room temperature, acidified to pH1 and the solid filtered off to give 5-methyl-6-(4-fluoro-phenylthio)-s-1,2,4-triazolo[1,5-a]pyrimidin-7-ol as a white solid which was used in the next stage without further purification.

#### Stage 2

The crude 5-methyl-6-(4-fluoro-phenylthio)-s-1,2,4-triazolo[1,5-a]pyrimidin-7-ol  
30 (0.39g) from Stage 1 and phosphoryl chloride (5ml) were refluxed for 23 hours and allowed to cool down to room temperature. The resulting red solution was poured carefully onto

crushed ice, extracted with chloroform, washed with water and dried over anhydrous magnesium sulphate. Removal of the solvent gave a red residue that was purified by column chromatography (silica gel eluted with ethyl acetate/hexane 1:1) and HPLC (eluting with ethyl acetate/hexane 2:5) to give the title compound (0.036g) as a white solid ( $M^+ = 295$ ).

5  $^1\text{H}$  nmr  $\delta$  2.8 (3H, s), 7.0 (2H, t), 7.2 (2H, m), 8.5 (1H, s) ppm.

#### EXAMPLE 5

This Example illustrates the preparation of (Compound No. 22, Table 1)

##### Stage 1

A solution of bromine (4.1ml) in glacial acetic acid (6ml) was added dropwise to a solution  
10 of 7-hydroxy-s-[1,2,4]triazolo[1,5-a]pyrimidin-5(1H)-one, (18.0g) in glacial acetic acid (600ml) with stirring at room temperature. After complete addition, the solution was stirred at room temperature for 3 hours. The solid was separated by filtration, washed with ethanol and air dried to give 5-methyl-6-bromo-s-triazolo[1,5-a]pyrimidin-7-ol (19.2g, 71% yield) as a pale white solid:  $M^+$  236; M.P.  $>256^\circ\text{C}$ .

##### 15 Stage 2

A mixture of 6-bromo-7-hydroxy-s- [1,2,4]triazolo[1,5-a]pyrimidin-5(1H)-one (10g), piperidine (7ml), potassium carbonate (5 g) in DMF (80ml) was stirred overnight at  $100^\circ\text{C}$ . The yellow thick suspension was cooled to ambient temperature and evaporated to dryness under reduced pressure. The residue was resuspended in ethanol at  $60^\circ\text{C}$  for about an hour.  
20 After filtration the mother liquor was evaporated to dryness to yield 6-N-piperidino-7-hydroxy-s-[1,2,4]triazolo[1,5-a]pyrimidin-5(1H)-one (4.9 g, 80%) as pale yellow solid:  $M^+$  299; M.P.  $255^\circ\text{C}$ ;  $^1\text{H}$  nmr ( $\text{D}_2\text{O}$ )  $\delta$  7.78 (1H, s) ppm.

##### Stage 3

Phosphoryl chloride (35ml) was added dropwise, with caution, to 6-N-piperidino-7-  
25 hydroxy-s- [1,2,4]triazolo[1,5-a]pyrimidin-5(1H)-one (3.5g). After complete addition the mixture was refluxed for 2 hours, cooled to room temperature and poured carefully with stirring onto crushed ice. The resulting red solution was extracted with diethyl ether, washed with water, dried and the solvent removed to give 5,7-dichloro-6-N-piperidino-s-triazolo[1,5-a]pyrimidine (3.60g, 70% yield) as an yellow oil.

30  $M^+$  272;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  1.48-1.75 (6H, m), 3.02-3.14 (4H, m), 8.48 (1H, s) ppm.

##### Stage 4

(S)-2,2,2-Trifluoro-1-methyl-ethylamine (830 mg) was added dropwise to a solution of 5,7-dichloro-6-piperidino-s-triazolo[1,5-a]pyrimidine (500 mg) in dry DMF (30 ml) at 70°C. The reaction was stirred for 12 hours, poured into ice-cold water and extracted with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulphate and the ether removed to give the title compound (448 mg, 70% yield) as a pale yellow solid:  $M^+$  349; M.P. 127°C.

#### EXAMPLE 6

This Example illustrates the preparation of (Compound No. 28, Table 1)

##### Stage 1

10 A mixture of 6-bromo-7-hydroxy-s [1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (5 g), 4-fluoro-phenol (2 g), potassium carbonate (2.5 g) in DMF (50ml) was stirred overnight at 100°C. The yellow thick suspension was cooled to ambient temperature and evaporated to dryness under reduced pressure. The residue was resuspended in ethanol at 60°C for about an hour. After filtration the mother liquor was evaporated to dryness to yield 6-(4-fluorophenoxy)-7-hydroxy-s- [1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (2.25 g, 48%) as pale yellow solid:

$M^+$  261,  $M^+$  263; M.P. >256°C;  $^1\text{H}$  nmr ( $\text{D}_2\text{O}$ )  $\delta$  7.18-7.24 (4H, m), 7.85 (1H, s) ppm.

##### Stage 2

20 Phosphoryl chloride (20 ml) was added dropwise, with caution, to 6-(4-fluorophenoxy)-7-hydroxy-s- [1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (2 g). After complete addition the mixture was refluxed for 3 hours, cooled to room temperature and poured carefully with stirring onto crushed ice. The resulting red solution was extracted with diethyl ether, washed with water, dried and the solvent removed to give 5,7-dichloro-6-(4-fluorophenoxy)-s-triazolo[1,5-a]pyrimidine (1.32 g, 57% yield) as a yellow solid:

25 M.P. 130°C;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  6.74-6.78 (2H, m), 6.94-7.04 (2H, m), 8.52 (1H, s) ppm.

##### Stage 3

(S)-2,2,2-Trifluoro-1-methyl-ethylamine (385 mg) was added dropwise to a solution of 5,7-dichloro-6-(4-fluorophenoxy)-s-triazolo[1,5-a]pyrimidine (255 mg) in dry DMF (30ml) at ambient temperature. The reaction was stirred for 12 hours, poured into ice-cold water and extracted with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulphate and the ether removed to give the title compound (286 mg, 89% yield) as a pale brown solid:  $M^+$  374; M.P. 156°C

30

## EXAMPLE 7

This Example illustrates the fungicidal properties of compounds of formula (I). The compounds were tested against a variety of foliar fungal diseases of plants. The technique employed was as follows.

5       Plants were either grown in John Innes Potting Compost (No.1 or 2) in 4cm diameter, 3.5cm depth minipots or on an artificial, cellulose based growing medium. The test compounds were individually formulated as a solution either in acetone or acetone/ethanol (1:1 by volume) which was diluted in reverse osmosis water to a concentration of 75 or 100ppm (that is, 0.75 or 1mg of compound in a final volume of 10ml) immediately before  
10   use. When foliar sprays were applied to monocotyledonous crops, TWEEN 20 (0.05% by volume) was added. TWEEN is a registered trade mark.

Individual compounds of formula (I) were applied as a foliar (Folr) application (where the chemical solution was applied to the foliage of the test plants by spraying the plant to maximum droplet retention); as a systemic (Syst) application (where the chemical  
15   solution, 10ml, was applied as a root drench treatment) or as a stem (Stem) application (where the chemical solution was applied to the stems of the test plants by spraying the plants to run off).

These tests were carried out against *Plasmopara viticola* (PLASVI) and *Uncinula necator* (UNCINE), on vines; *Phytophthora infestans lycopersici* (PHYTIN) and *Botrytis cinerea* (BOTRCI), on tomatoes; *Venturia inaequalis* (VENTIN), on apples; *Blumeria graminis f.sp. tritici* (ERYSGT), *Stagonospora nodorum* (LEPTNO) and *Puccinia triticina* (PUCCRT), on wheat; and *Pyricularia oryzae* (PYRIOR) and *Rhizoctonia solani* (RHIZSO), on rice. Each treatment was applied to two or more replicate plants for *Plasmopara viticola*, *Phytophthora infestans lycopersici*, *Botrytis cinerea*, *Uncinula necator* and *Venturia*  
20   *inaequalis* and in all tests where the cellulose growing medium was employed. In mini pot tests on *Blumeria graminis f.sp. tritici*, *Stagonospora nodorum*, *Puccinia triticina*, *Rhizoctonia solani* and *Pyricularia oryzae* two replicate pots each containing 6 to 10 plants were used for each treatment. The plants were inoculated with a calibrated fungal spore suspension one or two days before (Erad) or 6 hours, one day or two days after (Prot)  
25   chemical application.  
30

After chemical application and inoculation, the plants were incubated under high humidity conditions and then put into an appropriate environment to allow infection to

proceed, until the disease was ready for assessment. The *Blumeria graminis f.sp. tritici* plants were inoculated using a 'shake' inoculation technique. The *Uncinula necator* plants were inoculated using a 'blowing' inoculation technique. For *Plasmopara viticola*, the plants were reincubated under high humidity conditions for 24 hours prior to assessment. The time period  
5 between chemical application and assessment varied from five to fourteen days according to the disease and environment. However, each individual disease was assessed after the same time period for all compounds.

Assessments were performed on a single leaf of each of the two replicate plants for *Plasmopara viticola* and *Venturia inaequalis* and on each of two leaves on each of the  
10 replicate plants for *Phytophthora infestans lycopersici* and *Botrytis cinerea*. Assessments were performed on a single leaf of each of the three replicate plants for *Uncinula necator*. For *Blumeria graminis f.sp. tritici*, *Stagonospora nodorum*, *Puccinia triticina* and *Pyricularia oryzae* assessments were carried out collectively on the plants in each replicate pot or cellulose medium. For *Rhizoctonia solani*, the number of infected plants in each of two  
15 replicate pots was assessed.

The disease level present (that is, the percentage leaf area covered by actively sporulating disease) or percentage of infected plants per pot was assessed visually. For each treatment, the assessed values for all its replicates were meaned to provide mean disease values. Untreated control plants were assessed in the same manner.

20 The following are examples of the compounds tested that showed plant fungicidal activity against one or more of the diseases: compounds 1, 2, 3, 6, 21-25, 27, 28, 30, 31, 33-35 of Table 1.

#### EXAMPLE 8

This Example illustrates the fungicidal properties of compounds of formula (I), where the  
25 compounds were tested against a variety of foliar fungal diseases of plants in a leaf disk assay, with methods described below. Test compounds were dissolved in DMSO, and diluted into water to 200 ppm.

*Erysiphe graminis f.sp. hordei* (barley powdery mildew): barley leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to  
30 dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as preventive fungicidal activity.

*Erysiphe graminis f.sp. tritici* (wheat powdery mildew): wheat leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was  
5 assessed four days after inoculation as preventive fungicidal activity.

*Pyricularia oryzae* (rice blast): rice leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as  
10 preventive fungicidal activity.

*Botrytis cinerea* (grey mould): bean leaf disks were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as  
15 preventive fungicidal activity.

*Phytophthora infestans* (late blight of potato on tomato): tomato leaf disks were placed on water agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound  
20 was assessed four days after inoculation as preventive fungicidal activity.

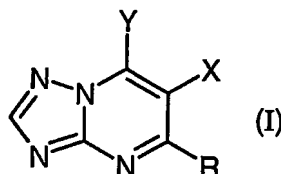
*Plasmopara viticola* (downy mildew of grapevine): grapevine leaf disks were placed on agar in a 24-well plate and sprayed a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was  
25 assessed seven days after inoculation as preventive fungicidal activity.

The following compounds from Table 1 gave greater than 60% control of disease: *Erysiphe graminis f.sp. hordei*, compounds 22, 25, 31, 34; *Erysiphe graminis f.sp. tritici*, compounds 22, 25, 34, 37, 49; *Pyricularia oryzae*, compounds 22, 25, 28, 29, 34, 38, 49, 57, 59; *Botrytis*  
30 *cinerea*, compounds 26, 49, 52, 59; *Plasmopara viticola*, compounds 29, 35, 38, 49, 54, 55, 56, 57; *Phytophthora infestans*, compounds 28; *Pythium ultimum*, compounds 52.



## CLAIMS

1. The use as a plant fungicide of a compound of the general formula (I):

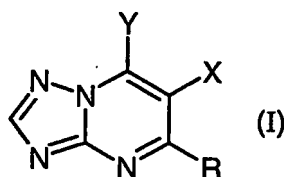


- wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X and Y are independently halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, di(C<sub>2-8</sub>)alkenylamino, di(C<sub>2-8</sub>)alkynylamino, C<sub>2-8</sub> alkenyl(C<sub>2-8</sub>)alkynylamino C<sub>2-8</sub> alkynyl(C<sub>1-8</sub>)alkylamino or C<sub>2-8</sub> alkenyl(C<sub>1-8</sub>)alkylamino arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino, heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino, morpholino or piperidino, or Y is hydroxy, provided that when X is C<sub>1-8</sub> alkoxy, aryloxy, morpholino or piperidino, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.
2. The use as a plant fungicide of a compound of the general formula (I) according to claim 1 wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X and Y are independently halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino or Y is hydroxy, morpholino or piperidino, provided that when X is other than halo, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.

3. The use as a plant fungicide of a compound of the general formula (I) according to claim 1 wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X is halo, C<sub>1-8</sub> alkylthio, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, 5 aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino; and Y is halo, hydroxy, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, 10 heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl (C<sub>1-8</sub> alkyl)amino, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.
- 15
4. The use as a plant fungicide of a compound of the general formula (I) according to any one of the preceding claims wherein R is H, halo or C<sub>1-4</sub> alkyl.
5. The use as a plant fungicide of a compound of the general formula (I) according to 20 any one of the preceding claims wherein when one of X or Y is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino the other 25 is halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, C<sub>1-8</sub> alkylamino, di(C<sub>1-8</sub>)alkylamino, or, in the case of Y, hydroxy.
6. The use as a plant fungicide of a compound of the general formula (I) according to 30 claim 1 wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X is halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, C<sub>1-8</sub> alkylamino or di(C<sub>1-8</sub>)alkylamino and Y is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino,

- di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)-alkylamino, heteroaryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, morpholino or piperidino; any of the foregoing alkyl moieties being optionally substituted with halo and any of the foregoing aryl or heteroaryl groups being optionally substituted with halo, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, cyano, nitro, amino, C<sub>1-4</sub> alkylamino or di(C<sub>1-4</sub>)alkylamino.
- 5
7. The use as a plant fungicide of a compound of the general formula (I) according to claim 1 wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano X is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)-alkylamino, or heteroaryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino; and Y is halo, hydroxy, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, C<sub>1-8</sub> alkylamino or di(C<sub>1-8</sub>)alkylamino; any of the foregoing alkyl moieties being optionally substituted with halo and any of the foregoing aryl or heteroaryl groups being optionally substituted with halo, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, cyano, nitro, amino, C<sub>1-4</sub> alkylamino or di(C<sub>1-4</sub>)-alkylamino.
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8. The use as a plant fungicide of a compound of the general formula (I) according to claim 1 wherein R is halo; X is phenoxy, phenylthio, heteroaryloxy, heteroarylthio, morpholino or piperidino; and Y is C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, di(C<sub>2-8</sub>)alkenylamino, di(C<sub>2-8</sub>)alkynylamino, C<sub>2-8</sub> alkenyl(C<sub>2-8</sub>)alkynylamino C<sub>2-8</sub> alkynyl(C<sub>1-8</sub>)alkylamino or C<sub>2-8</sub> alkenyl(C<sub>1-8</sub>)alkylamino; any of the foregoing alkyl, alkenyl, alkynyl, phenyl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.
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9. The use as a plant fungicide of a compound of the general formula (I) wherein R is halo; X is phenylthio, heteroaryloxy or heteroarylthio; and Y is halo; any of the foregoing phenyl or heteroaryl moieties being optionally substituted.

10. A compound of general formula (I):



- wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X and Y are independently halo, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino or Y is hydroxy, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted; provided that when X is other than halo, R and Y are not both halo, that when X is bromo and R is methyl, Y is not diethylamino or 3-(diethylamino)-propylamino, that when X is chloro and R is methyl, Y is not benzylamino and that when X is bromo or chloro and R is H or methyl, Y is not chloro or hydroxy.
11. A compound of general formula (I) wherein R is H, halo, C<sub>1-8</sub> alkyl or cyano; X is halo, C<sub>1-8</sub> alkylthio, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino; and Y is halo, hydroxy, C<sub>1-8</sub> alkoxy, C<sub>1-8</sub> alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C<sub>1-4</sub>)alkoxy, heteroaryl(C<sub>1-4</sub>)alkoxy, aryl(C<sub>1-4</sub>)alkylthio, heteroaryl(C<sub>1-4</sub>)alkylthio, C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, arylamino, aryl(C<sub>1-8</sub> alkyl)amino, heteroarylamino, heteroaryl(C<sub>1-8</sub> alkyl)amino, aryl(C<sub>1-4</sub>)alkylamino, aryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, heteroaryl(C<sub>1-4</sub>)alkylamino or heteroaryl(C<sub>1-4</sub>)alkyl(C<sub>1-8</sub> alkyl)amino, morpholino or piperidino; any of the foregoing alkyl,

alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted; provided that when X is bromo and R is methyl, Y is not diethylamino or 3-(diethylamino)-propylamino, that when X is chloro and R is methyl, Y is not benzylamino and that when X is bromo or chloro and R is H or methyl, Y is not chloro or hydroxy.

12. A compound of the general formula (I) as defined in claim 1 wherein R is halo; X is phenoxy, phenylthio, heteroaryloxy, heteroarylthio, morpholino or piperidino; and Y is C<sub>1-8</sub> alkylamino, C<sub>2-8</sub> alkenylamino, C<sub>2-8</sub> alkynylamino, di(C<sub>1-8</sub>)alkylamino, di(C<sub>2-8</sub>)alkenylamino, di(C<sub>2-8</sub>)alkynylamino, C<sub>2-8</sub> alkenyl(C<sub>2-8</sub>)alkynylamino C<sub>2-8</sub> alkynyl-(C<sub>1-8</sub>) alkylamino or C<sub>2-8</sub> alkenyl(C<sub>1-8</sub>)alkylamino; any of the foregoing alkyl, alkenyl, alkynyl, phenyl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.
13. A compound of the general formula (I) as defined in claim 1 wherein R is halo; X is phenylthio, heteroaryloxy or heteroarylthio; and Y is halo; any of the foregoing phenyl or heteroaryl moieties being optionally substituted.
14. A plant fungicidal composition comprising a fungicidally effective amount of a compound as defined in claim 1 and a suitable carrier or diluent therefor.
15. A method of combating or controlling phytopathogenic fungi which comprises applying to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or to any other plant growth medium, a fungicidally effective amount of a compound as defined in claim 1 or a composition as defined in claim 14.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 02/04734

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N43/90

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, EPO-Internal

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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

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